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POROUS METAL-ORGANIC FRAMEWORKS: FROM SYNTHESIS TO FUNCTIONAL PROPERTIES

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Abstract. Lying on the crossing of fundamental inorganic/organic chemistry and development of novel materials, metal-organic frameworks (MOFs) have become one of the most attractive research fields during the past two decades. MOFs can be self-assembled from a large number of metal ions/clusters with organic linkers and can be regarded as multifunctional materials due to a wide range of important properties. MOFs often combine properties caused by specific framework architecture, e.g. permanent porosity, selective gas sorption and separation, and chemical stability, with those ones related to the properties of inorganic building blocks, e.g. luminescence and magnetism. Here we describe our recent results on synthesis, structural characterization and investigation of multifunctional materials based on porous coordination polymers.[1–4]

For a series of microporous MOFs $[Li_2Zn_2(R\text{-}bdc)_3(bpy)]$ the CH_4 and CO_2 adsorption and relative selectivities have been investigated in detail, and interestingly, a fascinating interplay of luminescence properties with wavelength of excitation and nature of the host aromatic guest molecules has been observed. Moreover, such compounds demonstrate very high selectivity in the processes of separation of benzene and cyclohexane.

We also report two isostructural series of micro- (NIIC-10) and mesoporous (NIIC-20) zinc(II) – thiophene-2,5-dicarboxylate. The obtained microporous MOFs demonstrated excellent adsorption selectivity for CO_2/N_2 gas mixture, and in separation of benzene/cyclohexane mixtures both in gas and liquid phases. Most interestingly, the affinity of the porous MOF towards either benzene or cyclohexane could be rationally switched by the nature of the polyatomic alcohol.

The mesoporous NIIC-20 compounds feature high surface area and rarely observed inversed adsorption affinity for saturated hydrocarbon (ethane) over the unsaturated ones (ethylene, acetylene). The adsorption selectivity factors reach as much as 15.4 for C_2H_6/C_2H_4 and 10.9 for C_2H_6/C_2H_2 gas mixtures at ambient conditions, exceeding those for any other porous MOF reported so far. The remarkable combination of high adsorption uptakes and high adsorption selectivities makes the NIIC-20 series a new benchmark of porous materials designed for ethylene separation applications.

References

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